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1. Title of the Invention

Method for manufacturing embossed sheet

2. Claims

In a method for manufacturing a synchronous embossed sheet with conformity between printed pattern and irregular pattern, which comprises forming a layer of expandable synthetic resin composition on a base material, printing an optional pattern on the surface thereof with a printing ink containing a foaming inhibitor, forming a transparent or translucent synthetic resin layer thereon followed by heating expansion to make an irregular pattern emerge thereon, and forming a grained pattern on the surface by use of an optionally designed embossing roll, the average polymerization degree of the synthetic resin used for the expandable synthetic resin composition being set to 1200 or more, the average polymerization degree of the synthetic resin used for the transparent or translucent synthetic resin composition being set higher than the average polymerization degree of the synthetic resin used for the expandable synthetic resin composition by 100 or more, and the expansion rate being set to 4 times or less.

3. Detailed Description of the Invention

[Usable Field in Industry]

This invention relates to a method for manufacturing an excellently decorative embossed sheet with conformity between printed pattern and irregular pattern having a fine and sharp grained pattern on the surface, which is used as building material such as floor material, wall material or the like, vehicle sheet, bag, pouch, furniture or the like.

[Prior Arts]

Such an embossed sheet with conformity between printed pattern and irregular pattern is conventionally manufactured by a chemical embossing method of printing a pattern on the surface of an expandable synthetic resin layer by use of a printing ink containing a foaming inhibitor and/or a foaming accelerator and expanding it to make an irregular pattern emerge thereon, a synchronous embossing method of performing an embossing according to a printed pattern by use of an embossing roll, or the like. The chemical embossing method cannot represent fine and sharp irregularities although the printed pattern can be matched to the irregular pattern. The synchronous embossing can represent fine and sharp irregularities according to the shape of the embossing roll to be used, but has the problem of difficulty of pattern matching due to extension of sheet, mechanical conditions and the like because of the mechanical matching of the printed pattern to the irregular pattern, resulting in extremely low workability and a high of defective rate.

[Means to Solve the Problems]

This invention relates to a method for easily manufacturing a superbly decorative embossed sheet with conformity between printed pattern and irregular pattern having a fine and sharp grained pattern following the grained pattern of an embossing roll on the surface. Namely, in a method for manufacturing a synchronous embossed sheet with conformity between printed pattern and irregular pattern, which comprises forming a layer of expandable synthetic resin

composition on a base material, printing an optional pattern on the surface by use of a printing ink containing a foaming inhibitor, forming a transparent or translucent synthetic resin layer thereon followed by heating expansion to make an irregular pattern emerge thereon, and forming a grained pattern by use of an optionally designed embossing roll, the average polymerization degree of the synthetic resin used for the expandable synthetic resin composition is set to 1200 or more, the average polymerization degree of the synthetic resin used for the transparent or translucent synthetic resin layer is set higher than the average polymerization degree of the synthetic resin used for the expandable synthetic resin composition by 100 or more, and the expansion rate is set to 4 times or less.

As the base material used in this invention, releasable carriers are usable in addition to a woven fabric, knitted fabric, nonwoven fabric, paper or the like consisting of at least one of inorganic or organic fibers such as natural animal or vegetable fiber, asbestos, glass fiber, rock wool, pulp, synthetic fiber and the like, as occasion demands, mixed with a filler such as calcium carbonate, clay, aluminum hydroxide or the like or a resin binder, and these can be selectively used according to the use of an intended product. In addition to the above, the above woven fabric, knitted fabric, nonwoven fabric, paper or the like having a foamed or non-foamed sheet of synthetic resin laminated on the reverse side thereof (the opposite side to the surface for forming the expandable synthetic resin composition) can be used also as the base material of the synchronous embossed sheet according to this invention.

The layer of the expandable synthetic resin composition is formed of a thermoplastic synthetic resin, a chemical foaming agent thermally decomposed by heating to generate a gas, and a foaming assistant for promoting the decomposition of the foaming agent, and a generally used additive such as plasticizer, stabilizer, filler, antimold, viscosity reducer, coloring agent or the like

may be further used as occasion demands.

As the thermoplastic synthetic resin, any generally used synthetic resin such as vinyl chloride resin, acrylic resin, vinyl acetate resin, polyethylene, polypropylene, ethylene-vinylacetate copolymer resin, urethane resin or the like may be used, and the vinyl chloride resin is particularly preferred. The vinyl chloride resin referred herein include mixtures of polyvinyl chloride resin with other polymers as well as polyvinyl chloride resin and copolymers of vinyl chloride with other monomers, for example, ethylene, vinyl acetate, vinyl ether, maleate, acryl, urethane and the like. The average polymerization degree of the synthetic resin to be used is required to be 1200 or more. When the average polymerization degree is less than 1200, the melt viscosity of the expanded layer is reduced in heating embossing, so that the roughing of surface is caused by the rupture of expanded cells in the pressing by the embossing roll to make the embossing difficult.

As the foaming agent, those generally used are usable, and azodicarbonamide is particularly preferred. The addition quantity is preferably set to 0.5-5 parts by weight to 100 parts by weight of vinyl chloride resin.

As the expansion assistant for promoting the decomposition of the foaming agent, those generally used are usable according to the kind of the foaming agent. When the azodicarbonamide is used as the foaming agent, a zinc-based or lead-based foaming assistant serving also as stabilizer such as zinc acetate is preferably used.

As the plasticizer, a general plasticizer such as trimellitate-based plasticizer, epoxy-based plasticizer such as epoxidized soybean oil, various epoxy resins or the like, polyester-based polymeric plasticizer or the like is usable in addition to dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, didodecyl phthalate, butylbenzyl phthalate, diisodecyl phthalate, dihexyl phthalate,

didodecyl phthalate, diisononyl phthalate, dioctyl adipate, diisodecyl adipate, dibutyl sebacate, dioctyl sebacate, tributyl phosphate, tricresyl phosphate, triphenyl phosphate, trichloroethyl phosphate, trioctyl phosphate, diphenylcresyl phosphate and the like.

When the vinyl chloride resin paste is used as the expandable synthetic resin composition, a diluent or secondary plasticizer such as gasoline, octane, benzene, toluene, naphtha, dodecyl benzene derivative or the like and a generally used agent such as viscosity reducing agent or the like are used jointly with the plasticizer, as occasion demands, in order to reduce the viscosity.

The quantity of the plasticizer added is set to 20-100 parts by weight to 100 parts by weight of the vinyl chloride resin, and the diluent or secondary plasticizer and the viscosity reducing agent are preferably used within the ranges of 1-20 parts by weight and 0.1-5 parts by weight, respectively.

As the stabilizer, those generally used are usable. When the azodicarbonamide is used as the foaming agent, the zinc-based or lead-based stabilizer such as zinc oxide having the effect as foaming assistant and stabilizer is preferably used. The quantity of the stabilizer added is preferably set to the range of 0.5-7 parts by weight to 100 parts by weight of vinyl chloride resin.

As the filler, any one which doesn't cause a physical or chemical change such as melting, decomposition or the like at a working temperature is usable, including an inorganic filler such as calcium carbonate, magnesium carbonate, clay, talc, silica, diatomaceous earth, quartz sand, pumice powder, flake powder, mica powder, asbestos, aluminum hydroxide, aluminum oxide, aluminum sulfate, barium sulfate, calcium sulfate, glass ball, foamed glass ball, fly ash ball, volcanic glass hollow body (shirasu balloon) or the like, and an organic filler such as powdery fibrin (cellulose powder), polyvinyl alcohol fiber, cork powder, wood meal, thermosetting resin powder, thermosetting resin hollow ball or the like. The

addition quantity of the filler is preferably set to the range of 5-400 parts by weight to 100 parts by weight of vinyl chloride resin.

As the antimold, those generally used are usable, and an organic antimold never discoloring the vinyl chloride resin or arresting the foaming inhibiting effect by the foaming inhibitor such as 10,10'-oxybisphenoxyarsine, N-(fluorodichloromethylthio)-phthalimide, N-trichloromethylmercapto-4-cyclohexene-1,2-dicarboxyimide, 2, 4, 5, 6-tetrachloroisophthalonitrile or the like of 0.1-5 parts by weight to 100 parts by weight of vinyl chloride resin is preferably used, when effect persistence is required, in combination with an inorganic antimold such as barium methaborate of 1-30 parts by weight. Of course, the above antimolds may be used alone or in a combination of two or more thereof.

For the printing ink used in this invention, any printing ink generally used is usable. However, it is necessary to mix a generally used foaming inhibitor such as trimellitic anhydride, dithiocyanuric derivative or the like to at least one color of the printing ink for printing a pattern in order to inhibit the expansion of the expandable synthetic resin and form a recessed part. The addition quantity of the foaming inhibitor is properly regulated according to the intended depth of the recessed part, but preferably set within the range of 1-50 wt% to the printing ink.

For the transparent or translucent synthetic resin layer of this invention, any thermoplastic synthetic resin generally used is usable. Although the average polymerization degree of the synthetic resin to be used is preferably lower from the viewpoint of the reproducibility (embossing fitness) of an embossing pattern by the embossing roll and the foaming inhibiting effect by the foaming inhibitor, a clear print pattern cannot be obtained when it is lower than the average polymerization degree of the synthetic resin of the expandable synthetic resin composition because of remarkable foaming on the interface (or print

surface) between the transparent or translucent synthetic resin layer and the expandable synthetic resin layer by the influence of the decomposed gas of the foaming agent in expansion, and the surface smoothness is also deteriorated. Therefore, the average polymerization degree of the synthetic resin used for the transparent or translucent synthetic resin layer is preferably set higher than the average polymerization degree of the synthetic resin of the expandable synthetic resin composition by 100-4000. When the average polymerization degree of the synthetic resin used for the transparent or translucent synthetic resin layer is equal to or lower than the average polymerization degree of the synthetic resin of the expandable synthetic resin composition, the intended product cannot be provided because of the above reason, and when it exceeds 4000, not only the embossing fitness is deteriorated, but also the foaming inhibiting effect is remarkably deteriorated. Further, a generally used additive such as plasticizer, stabilizer, filler, or mat agent, antimold, viscosity reducing agent, coloring agent or the like is used as the occasion demands.

As the thermoplastic synthetic resin and various additives used as occasion demands, those used in the expandable synthetic resin composition can be used in the same mixing quantity. For the filler or mat agent, the filler used in the expandable synthetic resin composition can be used in 0.5-20 parts by weight to 100 parts by weight of the synthetic resin. When this mixing quantity exceeds 20 parts by weight, the synthetic resin layer is opaque so that the intended product cannot be provided.

The synchronous embossed sheet according to this invention can be obtained by forming the layer of the expandable synthetic resin composition on the sheet-like base material by a general method such as calendaring, extrusion, lamination, paste coating or the like; printing an optional pattern on the surface by use of the printing ink containing the foaming inhibitor in at least one color

thereof by a general method such as photogravure, flexo-printing, rotary screen printing, silk screen printing, or the like; forming a transparent or translucent synthetic resin layer on the surface by a general method such as calendaring, extrusion, lamination, paste coating or the like; heating and expanding the expandable synthetic resin composition at a temperature of the decomposition temperature of the foaming agent contained in the expandable synthetic resin composition to provide a sheet with conformity between printed pattern and irregular pattern; and then performing a heating embossing by use of an embossing roll having an optional grained pattern in a general embossing machine.

The embossing method include two methods of performing the heating expansion in an offline process having a foaming furnace separately set from the embossing machine followed by re-heating embossing and of performing the heating embossing in an inline machine having the embossing device set just after the foaming furnace, and each method is applicable. The offline embossing never causes the roughing of surface by the rupture of expanded cells by the pressing by the embossing roll since the foaming layer formed once is perfectly cooled, but requires the application of a heating condition such that the roughing of expanded cells is never caused by the decomposition and secondary expansion of the undecomposed foaming agent left in the foaming layer. When the embossing is performed inline just after the heating expansion, it is necessary to cool only the reverse side (the surface opposite to the embossing surface) as much as possible because the foaming layer is in a softened state and heat and emboss the surface under the condition never causing the secondary expansion of the undecomposed foaming agent left in the foaming layer. It is effective to perform a so-called clearance embossing having a clearance between the embossing roll and a rubber roll (backup roll) in embossing from the viewpoint of the prevention of the rupture

of expanded cells in the foaming layer. Since the clearance is slightly changed depending on the expansion rate of the foaming layer and the average polymerization degree of the synthetic resin for forming the foaming layer, it is necessary to set the clearance after confirming each of them. In this case, the expansion rate is required to be set to 4 times or less. The heating is performed with an expansion rate of foaming layer of 2.5 times or less and an average polymerization degree of the synthetic resin forming the foaming layer of 1200 or more under such a heating condition as never causes the secondary expansion of the foaming layer, and the embossing is performed with a pressure of the embossing roll of 2-3 kg/cm^2 (gauge pressure), whereby an intended synchronous embossed sheet can be easily obtained without any trouble such as rupture of expanded cells even if such a clearance is not provided. When the expansion rate of the foaming layer exceeds 2.5 times, the clearance is preferably provided according to the increase in expansion rate.

The heating in embossing is preferably performed by use of a generally used electric heater, infrared or far infrared heater, ceramic heater or the like.

Examples of the embossing roll used herein include one having a grained pattern formed by milling, etching, or electroforming and one having a grained pattern formed on a heat resisting synthetic resin such as silicon resin, and the like, and any one thereof is usable. Particularly, the electroforming embossing roll or synthetic resin-made roll such as silicon, which allows the emergence of just the original surface shape of a natural material, are preferably used, and the electroforming embossing roll is further preferable from the point of durability, shape retainability (less dimensional or shape change by temperature change), and coolability.

[Action and Effect]

According to this invention, a layer of expandable synthetic resin

composition is formed on the surface of a base material, an optional pattern is printed on the surface by use of a printing ink containing a foaming inhibitor, a transparent or translucent synthetic resin layer is formed thereon followed by heating expansion to make an irregular pattern synchronous to the printed pattern emerge thereon, and a grained pattern is formed on the surface by use of an optionally designed embossing roll by heating embossing, whereby a synchronous embossed sheet rich in design property, which has the conformity between the printed pattern and the irregular pattern and also has a fine and sharp grained pattern formed on the surface, can be easily and economically manufactured.

The average polymerization degree of the synthetic resin used for the expandable synthetic resin composition is set to 1200 or more, the average polymerization degree of the synthetic resin used for the transparent or translucent synthetic resin layer is set higher than the average polymerization degree of the synthetic resin sued for the expandable synthetic resin composition by 100 or more, and the expansion rate is set to 4 times or less, whereby an intended synchronous embossed sheet can be easily manufactured without causing any trouble such as rupture of expanded cells and surface roughing by the pressing by the embossing roll in the foaming layer heated and laid in a softened or melted state in the embossing by use of the embossing roll.

Further, a sheet excellent in complicated and fine decorative property which never existed in the past can be obtained by adding a design expression by multicolor printing with perfect conformity between printed pattern and irregular pattern by use of the printing ink partially containing the foaming inhibitor and a design expression by the grained pattern formed on the embossing roll, and this sheet is suitably usable as building material such as floor material, wall material or the like, vehicle sheet, bag, pouch, furniture or the like.

Preferred embodiments of this invention are described below in order to illustrate this invention in more detail, but this invention is never limited by these embodiments.

[Examples]

Examples 1-2, Comparative Example 1

By use of a test coater having an effective mechanical width of 450 m/m, each of expandable vinyl chloride resin pastes (II)-(IV) described in Table 1 was applied to the surface of an inorganic material paper 0.95 m/m thick mainly composed of glass fiber, pulp, inorganic filler and binder by a doctor knife so as to have a thickness of 0.45 m/m, and passed through a heating furnace set to 170°C at a rate of 2 m/min to heat and gel the expandable vinyl chloride resin pastes (II)-(IV). After the surface was subjected to multicolor photogravure of grained pattern (a joint part corresponding to the joint between wooden plates was printed with a printing ink containing an inhibitor), a transparent vinyl chloride resin paste (I) shown in Table 1 was applied thereto by a doctor knife so as to have a thickness of 0.3 m/m followed by passing through a heating furnace set to 170°C at a rate of 2 m/min to heat and gel the transparent vinyl chloride resin paste (I). Thereafter, it was passed through the heating furnace set to 190°C at a rate of 1.1-1.4 m/min so that the total thickness just after expansion was 2.2-2.5 m/m, and heating (under a heating condition as never causes the secondary expansion of the foaming layer) and embossing were performed by an electric heater by use of an electroforming embossing roll having a grained design just following natural wood thereon in an embossing device set inline just after the heating furnace [the clearance between the embossing roll and the backup roll was set to 1.9-2.1 m/m, the pressure of the embossing roll: 2 kg/cm^2 (gauge pressure)]. The result is shown in Table 2.

As is apparent from Table 2, the embossing work could be preformed

without any trouble by properly setting the embossing condition when the average polymerization degree of the vinyl chloride resin used for the expandable vinyl chloride resin paste composition was 1210 or 1455, and the resulting synchronous embossed sheet had a fine grained design similar to natural wood, and was suitable as floor material.

Table 1

(Unit: part by weight)

	Transparent VC resin paste (I)	Expandable VC resin paste		
		(II)	(III)	(IV)
PVC for paste P=3500	60	-	-	-
PVC for paste P=1100	-	70	-	-
PVC for paste P=1300	-	-	70	-
PVC for paste P=1650	-	-	-	70
VC coarse particle resin P=1000	40	30	30	30
Dioctyl phthalate	45	50	50	50
Epoxidized soybean oil	2	2	2	2
Secondary plasticizer	8	5	5	5
Stabilizer	3	-	-	-
Zinc flower (zinc oxide)	-	2	2	2
Azodicarbonamide	-	1.5	1.5	1.5
Coloring agent (beige)	-	3	3	3
Average polymerization degree in VC Paste	2500	1070	1210	1455

Table 2

		Example 1	Example 2	Comparative Example 3
Expandable VC resin paste		(III)	(IV)	(II)
Transparent VC resin paste		(I)	(I)	(I)
Total thickness after expansion (expansion rate)		2.5 m/m (2.8 times)	2.5 m/m (2.8 times)	2.3m/m (2.1 times)
Embossing condition	Clearance (m/m)	2.1	2.0	1.9
	Distance of heaters (5) (cm)	20	20	20
	Rate (expansion, embossing) (m/min)	1.3	1.1	1.4
Total thickness after embossing (m/m)		2.2	2.2	2.0
Result		O_{Δ}	O	×
		Surface roughing by rupture of expanded cells was partially caused, but the embossing work could be performed depending on proper condition set.	No surface roughing by rupture of expanded cells was caused, and the embossing work could be performed without any trouble.	Serious surface roughing by rupture of expanded cells was caused, and the embossing work could not be performed.

Examples 3-4, Comparative Examples 2-3

By use of a test coater with an effective mechanical width of 450 m/m, each of expandable vinyl resin pastes (D)-(E) shown in Table 3 was applied to the surface of an inorganic material paper 0.68 m/m thick mainly composed of glass fiber, pulp, inorganic filler and binder by a doctor knife so as to have a thickness of 0.63 m/m, and passed through a heating furnace set to 165°C at a rate of 2 m/min to heat and gel the expandable vinyl chloride resin pastes (D)-(E). The surface was subjected to multicolor photogravure of grained pattern (a joint part corresponding to the joint of wooden plates was printed with a printing ink containing an inhibitor), and each of transparent vinyl chloride resin pastes (A)-(C) shown in Table 3 was then applied thereto in a thickness of 0.18 m/m by a doctor knife so as to have combinations shown in Table 4 followed by passing it through a heating furnace set to 165°C at a rate of 2 m/min to heat and gel the transparent vinyl chloride resin pastes (A)-(C). Thereafter, it was passed through the heating furnace set to 195°C at a rate of 1.0-1.4 m/min so that the total thickness just after expansion (just after leaving the expansion furnace) was to 1.9-2.1 m/m, and heating and embossing were performed in an embossing device set inline just after the heating furnace by use of an electroforming embossing roll having a grained design just following natural wood by an electric heater. [Electric heater: the heating condition as never causes the secondary expansion of the foaming layer; clearance between embossing roll and backup roll: 0 (non); pressure of embossing roll: 2 kg/cm^2 (gauge pressure)]

The result is shown in Table 4.

Table 3

(Unit: parts by weight)

	Transparent VC resin paste			Expandable VC resin paste	
	(A)	(B)	(C)	(D)	(E)
PVC for paste P=1700	60	-	-	-	-
PVC for paste P=1950	-	60	-	-	-
PVC for paste P=3500	-	-	60	-	-
PVC for paste P=1100	-	-	-	70	-
PVC for paste P=1650	-	-	-	-	70
VC coarse particle resin P=1000	40	40	40	30	30
Dioctyl phthalate	33	33	45	50	50
Epoxidized soybean oil	2	2	2	2	2
Secondary Plasticizer	6	6	8	8	8
Stabilizer	3	3	3	-	-
Zinc flower (zinc oxide)	-	-	-	4	4
Azodicarbonamide	-	-	-	1	1
Coloring agent (beige)	-	-	-	3	3
Byk-4010 *1	2	2	-	-	1
Resin average polymerization degree in VC paste	1420	1570	2500	1070	1455

*1 Viscosity reducing agent made by

Table 4

		Example 3	Example 4	Comp. Example 2	Comp. Example 3
Expansible VC resin paste		(E)	(E)	(E)	(D)
Transparent VC resin paste		(B)	(C)	(A)	(C)
Total thickness just after expansion (expansion rate) (m/m)		2.1 (2.0 times)	2.1 (2.0 times)	1.95 (1.7 times)	2.0 (2.0 times)
Embossing condition	Clearance (m/m)	0	0	0	0
	Distance of heaters (5) (cm)	30	30	30	30
	Temp (°C) of sheet base material reverse side just before embossing	130	130	130	127
	Rate (expansion, embossing) (m/min)	1.0	1.0	1.0	1.4
Total thickness after embossing (m/m)		2.0	2.0	1.90	1.92
Result		○	○	×	×
		A synchronous embossed sheet with a fine design following the grained pattern of the embossing roll was obtained without surface roughing by rupture of expanded cells in embossing. The surface roughness after expansion was slightly poorer than in Example 4, and the surface was also slightly glossy.	A synchronous embossed sheet with a fine design following the grained pattern of the embossing roll was obtained without surface roughing by rupture of expanded cells in embossing. Surface flatness and gloss after expansion were satisfactory.	A large number of small bubbles were formed in the interface between the expansion layer and the transparent layer after expansion, and transparency and surface smoothness were deteriorated.	Breakage of expanded cells was caused by the pressing by the embossing roll in expansion to cause a serious surface roughing, and the intended synchronous embossed sheet was not obtained.

As is apparent from Table 4, the vinyl chloride resin having an average

polymerization degree of 1455 was used for the expandable vinyl chloride resin paste, and the vinyl chloride resin having an average polymerization degree higher than the vinyl chloride resin used for the expandable vinyl chloride resin paste composition by 100 or more was used for the transparent vinyl chloride resin layer to be formed through printing, whereby the deterioration of transparency and surface smoothness by generation of bubbles in the interface between the foaming layer and the transparent layer could be prevented, and the expansion rate was set to about 2 times or less, whereby the embossing work could be performed without any trouble such as the rupture of expanded cells by the pressing by the embossing roll even if the clearance between the emboss roll and the backup roll is 0 (no clearance is provided). Further, the resulting synchronous embossed sheet had a fine and sharp grained pattern similar to natural wood and was suitable as floor material.